

(12) JAPANESE PATENT OFFICE  
(19) PATENT JOURNAL (A)  
(11) KOKAI PATENT APPLICATION NO. 2001-139514

- (51) Int. Cl.<sup>7</sup>: C 07 C 51/43  
B 01 D 3/06  
C 07 C 63/26  
// C 07 B 61/00
- (21) Application No.: Hei 11[1999]-325066
- (22) Application Date: November 16, 1999
- (43) Publication Date: May 22, 2001
- No. of Inventions: 4 (Total of 5 pages; OL)
- Examination Request: Not requested
- (54) Title: METHOD FOR MANUFACTURING AROMATIC DICARBOXYLIC ACID
- (72) Inventor: Naoki Noguchi  
Kurosaki Business Office, Mitsubishi Chemical  
Industries Ltd.  
1-1 Shiroseki, Kurosaki, Yahatanishi-ku,  
Kitakyushu-shi, Fukuoka-ken
- (72) Inventor: Masaru Nishio  
2-12-2 Takamidai, Yahatanishi-ku, Kitakyushu-shi,  
Fukuoka-ken
- (72) Inventor: Toshiya Iwasaki  
Kurosaki Business Office, Mitsubishi Chemical  
Industries Ltd.  
1-1 Shiroseki, Kurosaki, Yahatanishi-ku,  
Kitakyushu-shi, Fukuoka-ken

- (71) Applicant: 000005968  
Mitsubishi Chemical Industries Ltd.  
2-5-2 Marunouchi, Chiyoda-ku, Tokyo-to
- (74) Agent: 100103997  
Akeshi Hasegawa, patent attorney

[There are no amendments to this patent application.]

(57) Abstract

Purpose: To provide an industrially very economical method that does not require a dryer and that can reduce the energy used for drying, particularly a method for manufacturing terephthalic acid by the liquid-phase oxidation of para-xylene.

Solution means: A method for obtaining an aromatic dicarboxylic acid, characterized by the fact that in a method for manufacturing an aromatic dicarboxylic acid that obtains an aromatic dicarboxylic acid as a product by removing the reaction medium from a slurry obtained by subjecting a dialkyl aromatic hydrocarbon to a liquid-phase oxidation in the reaction medium by molecular oxygen, the above-mentioned slurry is separated into a solid and a liquid under pressurization; the aromatic dicarboxylic acid obtained as a solid phase is flashed into a separating tank held at a pressure lower than the above-mentioned pressurization without reheating, so that the reaction medium is removed.

Claims

1. A method for obtaining an aromatic dicarboxylic acid, characterized by the fact that in a method for manufacturing an aromatic dicarboxylic acid that obtains an aromatic dicarboxylic acid as a product by removing the reaction medium from a slurry obtained by subjecting a dialkyl aromatic hydrocarbon to a liquid-phase oxidation in the reaction medium by molecular oxygen, the above-mentioned slurry is separated into a solid and a liquid under pressurization; with the aromatic dicarboxylic acid obtained as a solid phase being flashed into a separating tank held at a pressure lower than the above-mentioned pressurization without reheating, so that the reaction medium is removed.

2. The method for obtaining an aromatic dicarboxylic acid of Claim 1, characterized by the fact that the temperature of the liquid-phase oxidation of the dialkyl aromatic hydrocarbon and the solid phase of the separating tank inlet is set to a range of 140-210°C.
3. The method for obtaining an aromatic dicarboxylic acid of Claim 1 or 2, characterized by the fact that a discharge valve is used for flashing into the separating tank.
4. The method for obtaining an aromatic dicarboxylic acid of any of Claims 1-3, characterized by the fact that the dialkyl aromatic hydrocarbon is para-xylene; with the aromatic dicarboxylic acid being terephthalic acid.

#### Detailed explanation of the invention

[0001]

##### Technical field of the invention

The present invention pertains to an economically favorable method for manufacturing an aromatic dicarboxylic acid by eliminating the dryer size and reducing energy used for drying, when an aromatic dicarboxylic acid is manufactured by subjecting a dialkyl aromatic hydrocarbon to a liquid-phase oxidation, particularly when terephthalic acid is manufactured by subjecting para-xylene to liquid-phase oxidation.

[0002]

##### Prior art

Usually, in manufacturing terephthalic acid, it is common to oxidize para-xylene as a raw material in the liquid phase by molecular oxygen, using a metal salt of cobalt or manganese and bromine as catalysts along with a fatty acid such as acetic acid as a reaction medium. After this manufacturing process, as a purifying process, a water slurry is formed and terephthalic acid with a higher purity is obtained by hydrogenation purification, or terephthalic acid with a higher purity is obtained by an additional oxidation at a temperature higher than that of the oxidizing process, without going through the hydrogenation purification process. In any of the manufacturing processes of terephthalic acid, it is inevitable to separate the terephthalic acid product from the acetic acid (may also include a slight amount of water) used as a reaction medium and to draw it out in a dried powder state.

[0003] In other words, it was confirmed that the acetic acid was removed from the terephthalic acid cake containing the acetic acid by flashing at a high temperature and high pressure, so that

the cake was dried. In order to dry the terephthalic acid, a method that removes the liquid from the terephthalic acid by a separator and that dries the terephthalic acid with steam, etc., used as a heating medium in a noncondensable gas flow such as nitrogen in a rotary dryer has been adopted. According to this method, the amount of residual liquid of the reaction medium in the terephthalic acid after drying can be controlled to about 0.1 wt%. However, in this drying method, the drying rate is slow, the residence time in the dryer is long, the apparatus is large in scale, and the terephthalic acid is fixed to the inside of the dryer and the pipe of the heating medium. Thus, much effort is required for maintenance. Furthermore, a large amount of energy is consumed in the steam of the heating medium used for drying. As a method for drying the terephthalic acid without using a dryer, a method described in Japanese Kokai Patent Application No. Sho 55[1980]-164650 is proposed. In this method, the reaction medium such as acetic acid is vaporized by heating a slurry of terephthalic acid and acetic acid, so that the terephthalic acid as a solid part and the vaporized acetic acid, etc., are separated. In this method, a large amount of energy is required for vaporizing acetic acid, etc. Also, in a method that substitutes the solvent with water as proposed in Japanese Kokai Patent Application No. Hei 10[1998]-36313, the dryer can be eliminated; however, in separating the acetic acid and the water, a large energy is required in the distillation column, etc.

[0004]

#### Problems to be solved by the invention

These inventors repeatedly reviewed the above problems in earnest to eliminate the dryer in manufacturing terephthalic acid and to reduce the energy used in drying. As a result, it was discovered that after para-xylene was subjected to a liquid-phase oxidation in an oxidizing process, it was separated into a solid and a liquid at a high temperature and high pressure and the cake containing a slight amount of solvent separated was flashed at lower pressure, so that the acetic acid and vaporized water were more effectively removed. Then, the present invention was completed.

[0005]

#### Means to solve the problems

In other words, the essence of the present invention is a method for obtaining an aromatic dicarboxylic acid, characterized by the fact that in a method for manufacturing an aromatic dicarboxylic acid that obtains an aromatic dicarboxylic acid as a product by removing the reaction medium from a slurry obtained by subjecting a dialkyl aromatic hydrocarbon to a liquid-phase oxidation in the reaction medium by molecular oxygen, the above-mentioned slurry is separated into a solid and a liquid under pressurization; the aromatic dicarboxylic acid obtained

as a solid phase is flashed into a separating tank held at a pressure lower than the above-mentioned pressurization without reheating, so that the reaction medium is removed.

[0006]

#### Embodiment of the invention

Next, the present invention is explained in detail. In the present invention, para-xylene is mentioned as the dialkyl aromatic hydrocarbon. As the reaction medium, a lower aliphatic carboxylic acid is preferable, and specifically acetic acid can be mentioned. In the present invention, the liquid-phase oxidation reaction of said dialkyl aromatic hydrocarbon in the reaction medium can be carried out according to an ordinary method; usually, 90 wt% or more of the para-xylene is oxidized in the liquid phase to terephthalic acid by a gas containing molecular oxygen in the presence of a catalyst containing heavy metals such as cobalt, iron, and manganese, preferably a heavy metal salt and bromine. Next, the case wherein acetic acid is used as the reaction medium in the manufacture of terephthalic acid is described as an example; however, the present invention is not particularly limited to this case. The amount of acetic acid catalyst in the reaction medium used in the liquid-phase oxidation is usually 2-6 weight times that of the para-xylene. In said acetic acid solvent, a slight amount such as 10 wt% or less of water may also be included. As the gas containing molecular oxygen, air, oxygen diluted with an inert gas, oxygen-enriched air, etc., are used, and the air is usually used in terms of the facility and cost.

[0007] The catalyst used in the liquid-phase oxidation includes cobalt, manganese, and bromine; as detailed examples, cobalt acetate, cobalt naphthenate, cobalt bromide, etc., can be mentioned as the cobalt compounds. As the manganese compounds, manganese acetate, manganese naphthenate, manganese bromide, etc., can be mentioned, and as the bromide compounds, hydrogen bromide, sodium bromide, cobalt bromide, manganese bromide, tetrabromoethane, etc., can be mentioned. These compounds may also be used together. The amount of catalyst used is 120-3,000 wt ppm, preferably 200-2,000 wt ppm, with respect to the acetic acid as calculated in terms of cobalt metal. The amount of manganese component used is 0.001-0.4 times the atomic ratio to the cobalt. Also, the absolute amount of manganese component used is usually 1-250 wt ppm, preferably 5-200 wt ppm, with respect to the acetic acid as calculated in terms of manganese metal. The amount of bromine component used is 0.1-5 times, preferably 0.2-2 times, the atomic ratio to the cobalt. If the amount of catalyst used is out of the above-mentioned range, the purity or permeability of the terephthalic acid obtained is insufficient, or the acetic acid combustion is increased, so that the effect cannot be obtained. In particular, the amount of manganese component used is important; if the atomic ratio to the cobalt is less than

0.001 times, the reactivity is greatly lowered, and if the atomic ratio is more than 0.4 times, a precipitate of the manganese component is generated and mixed into the terephthalic acid, so that the quality of the terephthalic acid product is deteriorated, or the loss of the acetic acid is increased.

[0008] The reaction is preferably applied under a reaction temperature of 140-210°C, preferably 170-200°C, and especially preferably 175-195°C. If the reaction temperature is lower than 140°C, the reaction velocity is lowered, and if the reaction temperature is higher than 210°C, the amount of loss due to the combustion of the acetic acid solvent is increased, which is not preferable. The reaction pressure is that at which the mixture can retain the liquid phase at at least the reaction temperature, or a higher level, and it is usually 0.2-5 MPa. The reaction is usually continuously carried out, and the reaction time (average residence time) is 30-300 min. The moisture concentration in the reaction parent solution is usually 5-25 wt%, preferably 7-20 wt%, and the moisture concentration can be adjusted by discharging the volatilized gas in the reactor and by discharging (purging). Usually, the reactor used in the present invention has a tank with a stirrer, but the stirrer is not required. A bubble tower type may also be adopted. A cooler is installed at the upper part of the reactor, and a port for supplying the gas containing molecular oxygen is installed at the lower part. The gas containing molecular oxygen supplied from the lower part is utilized in the oxidation reaction and discharged as a gas component accompanied by a large amount of acetic acid vapor from the reactor, with the acetic acid being condensed and separated by a reflux cooler and discharged as an oxidized exhaust gas. The condensed solution is partially purged to the system outside, and the rest is refluxed to the reactor.

[0009] In the present invention, in applying the oxidation reaction of para-xylene, as described in Japanese Kokoku Patent No. Hei 5[1993]-32381, the oxidized exhaust gas obtained by condensing and removing the condensable component from the gas discharged from the reactor is branched into two flows. One of them is discharged to the system outside, and the other may be continuously circulated and supplied to the reactor. In the present invention, after the above-mentioned oxidizing reaction, the solid-liquid separation may be immediately carried out; however, if necessary, an additional treatment may also be carried out. As said additional treatment, for example, it is effective to additionally oxidize (hereinafter, referred to as "low-temperature additional oxidation") the reaction mixture of the above-mentioned oxidizing reaction (first reaction zone) in a second reaction zone held at a temperature lower than the reaction temperature (usually, 140-190°C) of the first reaction zone without supplying para-xylene. The amount of gas containing molecular oxygen supplied to said second reaction zone is

usually about 1/5-1,000 of the amount supplied to the oxidizing reaction in the first reaction zone, and the treatment time is 5-120 min. As another method of the additional treatment, it is also effective to additionally oxidize the above-mentioned oxidation reaction mixture without supplying para-xylene in a reaction zone (third reaction zone) at a temperature higher than the first reaction zone (hereinafter, referred to as "high-temperature additional oxidation"). The temperature of said third reaction zone is usually 210°C or higher, preferably 220-280°C. The amount of gas containing molecular oxygen supplied to said high-temperature additional oxidation is usually about 1/5-1/1,000 of the initial oxidation reaction.

[0010] The reaction mixture after the oxidation reaction, or the low-temperature additional oxidation or high-temperature additional oxidation as an additional treatment process, may be immediately subjected to a solid-liquid separation after each process, or may also be subjected to a solid-liquid separation through a precipitation treatment process. As an apparatus for applying said solid-liquid separation, a decanter, centrifugal separator, vacuum belt filter, drum filter, etc., are used, but it is not limited to them. After said solid-liquid separation, the reaction medium attached to the surface of the terephthalic acid is substituted by acetic acid containing water, and is washed. For the washing, a suspension washing tank is installed; the solid-liquid separation may be applied after washing, or the washing and the solid-liquid separation may also be applied at the time of the above-mentioned one-stage operation. In consideration of the reduction of the apparatus, the one-stage washing and separation is preferable. As a liquid used for the washing, fresh acetic acid may be used; however, a liquid condensed by the reactor or the condenser of the upper part of the low-temperature additional oxidation tank may also be used. As the important operation factors in the present invention, the conditions for applying the above-mentioned washing and solid-liquid separation are set to a pressure region higher than normal pressure, preferably 19.6 kPa (gauge pressure) or more, and more preferably 49 kPa (gauge pressure) or more, and a temperature preferably 140°C or higher, more preferably 165°C or higher, and especially preferably 170°C to the low-temperature additional oxidation temperature. At the same time, the separated wet cake (terephthalic acid containing a slight amount of reaction medium) is sometimes flashed (rapidly discharged from a high pressure to a low pressure) into a separating tank (hereinafter, referred to as "flashing tank") in a pressure region lower than the pressure of the solid-liquid separation without heating from the outside. In other words, using the vapor pressure of the high-temperature solvent during the pressurized separation, drying is carried out. The pressure of the flashing tank is usually normal pressure; however, pressurization or reduced pressure may also be adopted unless the vaporized component is condensed. The temperature of the flashing tank is not particularly limited; however, in order to obtain the product in a drier state, a high temperature, preferably a range from 100°C to the temperature of

the pressurized separation, is adopted. The pressure difference before and after flashing is preferably 19.6 kPa (gauge pressure) or more, more preferably 49 kPa (gauge pressure) or more.

[0011] As a valve used in the flashing tank inlet, a discharge valve is preferably used; however, any valve may be used as long as a high-concentration slurry can be continuously supplied. The reaction medium vaporized in the flashing tank is removed along with the noncondensable inert gas such as nitrogen, and the reaction medium may be recovered by cooling and condensing said gas and re-supplied to the reactor or sent to a water recovery process. On the other hand, the inert gas from which the reaction medium is removed can be reused as an accompanying gas. The dried terephthalic acid obtained in this manner may be transferred at high energy to a silo and temporarily stored, or may also be immediately transformed into an aqueous slurry and sent to a hydrogenation purification process. Next, referring to the figure, an example of the detailed embodiment of the present invention is explained. Figure 1 is an outlined diagram showing an example of the process in the present invention.

[0012] First, the catalyst, reaction medium, and para-xylene are supplied to an oxidation reactor 3 from a line 1, and molecular oxygen is supplied from a line 2. The solution after the oxidizing reaction is transferred to a low-temperature additional oxidizing tank 5 by a line 4. A small amount of molecular oxygen is supplied to the low-temperature additional oxidizing tank by a line 6. After the low-temperature additional oxidation, the slurry is transferred to a pressurized solid-liquid separator 9 through a line 7. The reaction medium in the slurry is separated through a line 10 by said separator 9, and the remaining cake is washed with part (extracted and supplied by the line 8) of a solution, in which the gas generated by the reactor 3 is condensed, and is re-subjected to the solid-liquid separation (the line for the liquid separated is 11). The reaction medium (line 10) obtained by the first-stage separation and mainly the washing liquid (line 11) obtained by the second-stage separation are recycled to the reactor 3 through a line 12. Part of the liquid passing through the line 12 is passed through a line 13 and transferred to a water separation process. The cake after the pressurized separation and the washing separation is flashed to a flashing tank 15 from a discharge valve 14. Nitrogen is sent to the gas-phase part of the flashing tank 15 from a line 16 and is discharged along with the reaction medium vaporized in the flashing tank 15 from a line 17. The discharged gas is cooled, then a condensed liquid 18 is supplied to the reactor 3. A gas phase 19 is re-transferred to the line 16 and reused. Sometimes, the dried terephthalic acid discharged from the flash tank 15 is transferred to a slurry-forming tank, for instance, transformed into a slurry, and transferred to a hydrogenation purification process.



[0013]

## Application example

Using an apparatus shown in Figure 2, a model experiment was carried out under the following conditions. In other words, in the constitution of the apparatus of Figure 2, a sample holder 21 capable of applying pressure corresponds to the pressurized solid-liquid separator 9 in Figure 1, a ball valve 23 is used instead of the discharge valve 14, and the flashing tank 15 corresponds to a flashing tank 24. Using the apparatus of Figure 2, as shown in the following Table I, the temperature and pressure of the sample holder 21 was changed, and a cake 22 containing water and acetic acid in the sample holder was flashed to the flashing tank 24 through the ball valve 23. The liquid content in the cake 22 containing water and acetic acid was obtained by the following equation. The liquid composition (weight ratio) in the cake 22 containing said water and acetic acid is acetic acid: water = 80:20. Also, the flashing tank 24 is set to normal pressure and 15°C. In other words, it was confirmed that the acetic acid was removed from the terephthalic acid cake containing acetic acid by flashing at a high temperature and high pressure, so that the cake was dried.

[0014]

(Expression 1) Liquid content (%) in the cake 22 =  $\text{liquid} / (\text{dried cake} + \text{liquid}) \times 100$

[0015]

Table 1

	Temperature (°C)	Pressure (MPs)	Initial liquid content (%)	Liquid content after flashing (%)
Application Example 1	172	0.8	19.14	1.26
Application Example 2	192	1	20.41	2.81

[0016]

## Effects of the invention

According to the present invention, especially in the method for manufacturing terephthalic acid by a liquid-phase oxidation of para-xylene, since no dryer is required and the energy used in drying can be reduced, this method is industrially very economical.

[0017]

Brief description of the figures

Figure 1 is an outlined diagram showing a process example for applying the present invention.

Figure 2 is an outlined diagram showing an example of a flashing tank effective for applying the present invention.

Explanation of symbols:

1, 2, 4, 6, 7, 8, 10, 11, 12, 13, 16, 17, 18, 19 Pipes

a, b, c Heat exchangers

3 Oxidation reactor

5 Low-temperature additional oxidation reactor

9 Pressurized separation and washing machine

14 Discharge valve

15 Flashing tank

21 Sample holder

22 Cake containing water and acetic acid

23 Ball valve

24 Flashing tank

PG Pressure gauge

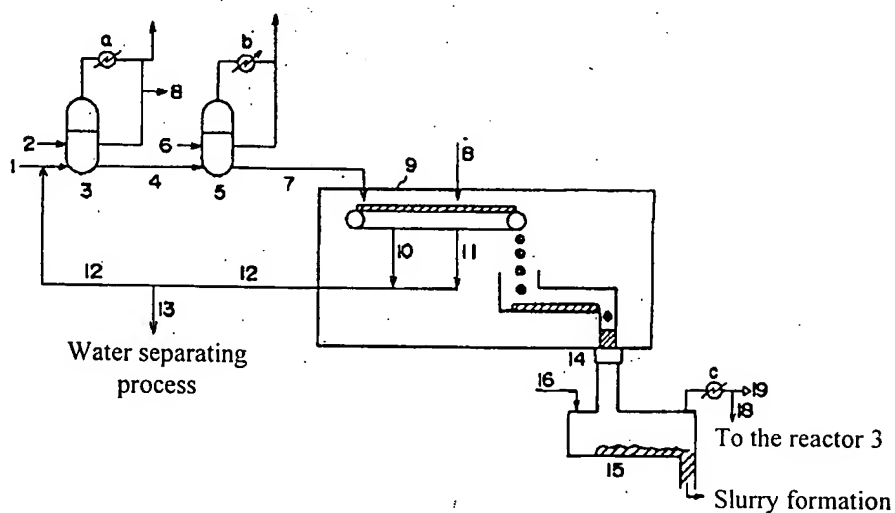


Figure 1

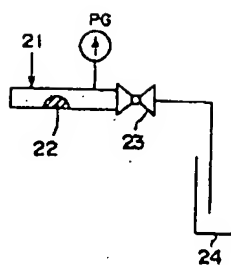


Figure 2



*...the height of Excellence...*

JAPANESE PATENT APPLICATION NO. 2001-139514  
METHOD FOR MANUFACTURING AROMATIC DICARBOXYLIC ACID

Translated from Japanese into English  
by Phoenix Translations Code No. 51-4412

2110-A WHITE HORSE TRAIL, AUSTIN, TX 78757 Phone: (512) 343-8389  
Toll-free: 877-452-1348, Fax: (512) 343-6721, Email: phoenixtranslations@ev1.net

Customer P.O. No.: None Given